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Some New Organic Complexes of Wolfram

by

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Some New Organic Complexes of Wolfram

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ABSTRACT

This study describes work on coordination chemistry which was undertaken as part of nitrogen fixation.

Dinuclear complexes of suitable structure might be capable of reacting with nitrogen .A possible mononuclear complex could also be favourable. In order to test these idea a number of wolfram complexes have been prepared and studied.

Since a good solvent has not been found they have not been tried for nitrogen fixation.

INTRODUCTION

Certain metals, for example mangenese, iron, cobalt, copper and molybdenum are often found in small (sometimes very small) amounts in living cells, and careful investigation has usually shown that those metals have very specific roles to play in particular enzymatic reactions. Sometimes the metal is bound to the enzyme itself more or less tightly; often it exists in the cell as a stable organic complex. Although probably the majority of enzymes function without a metal ion, the number which require one, especially a transition metal is considerable.

The main reasons are probably the readiness of such metal ions to form complexes in which the metal is joined to a number of atoms by bonds which are stable and can act as an oxidizing or reducing agents.

Wilson and his co-workers(1) have shown that Nitrogenase play important part in the fixation of atmospheric nitrogen. It is now generally accepted that, in free-living bacteria at least, all nitrogen fixed is in the form of ammonia immediately before its conversion to amino acids(2). The redox reactions which thus take place in nitrogen molecules are done by transition-metal ions which are well known for the readiness with which they undergo addition, removal or redistribution of electrons in the partly filled d-shell. The coordination chemistry of Molybdenum(3,4), Iron(5), Manganese(6), Cobalt(7), Wolfram(8) is thus clearly of interest in connection with nitrogen fixation.

Since nitrogenase has not been isolated the evidence concerning its metal requirement is indirect. However, many experiments have shown molybdenum is essential to a variety of nitrogen-fixing organizms (9,10,11,12,13,14). It has been shown that growth in the absence of fixed forms of nitrogen is especially dependent on molybdenum whereas growth on ammonium salts is generally independent of Mo (10,11,13,14)growth on nitrate shows a reduced molybdenum requirement (15). Vanadium and wolfram can replace molybdenum in some species (14) but wolfram has also been observed to cause inhibition, competitive with the molybdenum activation (15).

Concerning the actual way in which metal ions might be involved in the activation of nitrogen, it has been suggested (16, 17). that the presence of two metal atoms close together may be especially favourable. Winfield (17) is led to this conclusion partly from the mode of chemisorption of N_2 molecules on iron and wolfram surfaces.

In any event, it has been assumed for the purpose of this research that nitrogenase activity is associated with chealeted metal ions. Though reaction of N_2 with a single metal atom can not of course be neglected as a possibility, a dinuclear complex could be the most promising one.

Consequently it has been attempted to prepare some new dinuclear complexes of wolfram with some organic ligands which contain oxygen, nitrogen and their coordination properties were studied. Since a good solvent has not been found they have not been tried for nitrogen fixation impressively.

WOLFRAM COMPLEXES

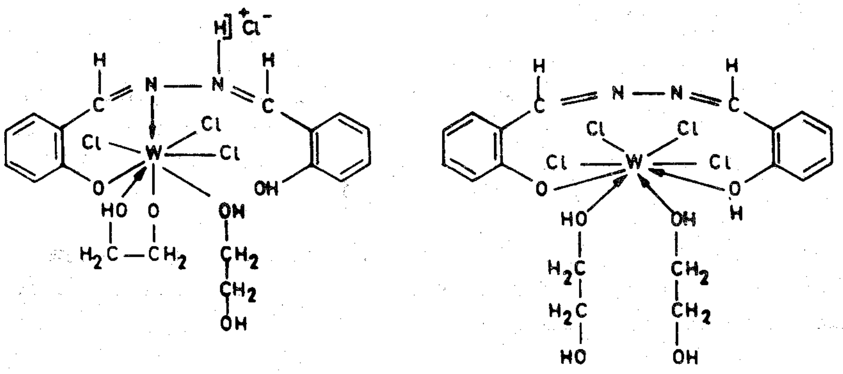
In this study some wolfram complexes have been prepared with the compounds containing oxygen and nitrogen ligands, like salicylaldazine, *β* -oxy *α*- naphthaldazine, *α*- picolinic acid, salicylaldehyde, *β*- oxy *α*- napthaldehyde and dimethyl glyoxime. As the oxidation number six is the most stable for wolfram (18) WCl_6 was used for the preparation of complexes.

The structures of the complexes throughout this study have been established by the microanalytical result, coordination rules, spectrophotometric and magnetic susceptibility measurements. Magnetic susceptibility measurements were made on a Gooy type magnetic balance and structural corrections were made according to Selwood (19 20).

Tetracholoro-wolfram V salicylaldazine - bis ethanediol:

Terent'ev and E.G. Rukhadze (21) prepared the complexes of salicylaldazine with Copper and Nickel and found that they are dinuclear. All attempts made to prepare dinuclear wolfram complex with salicylaldazine failed and instead a mononuclear complex has been obtained.

A complex which can be represented by the formula I or II was prepared from salicylaldazine and WCl_6 in dry dioxane. As the reaction between WCl_6 and salicylaldazine is very slow, a small amount of ethanediol which also served to get a good yield was added.

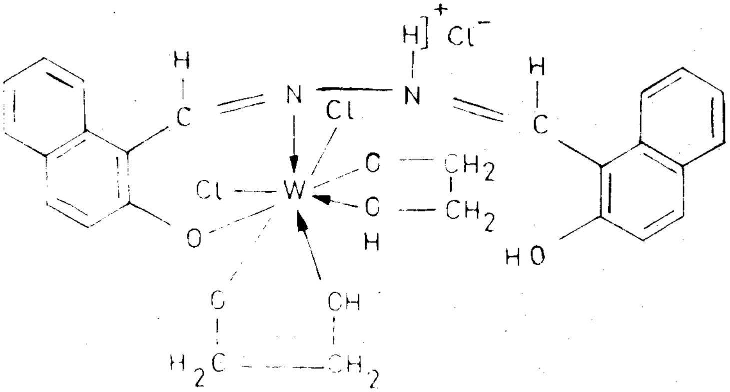


I—II. Pale green crystals M.P. 118°C (Decomp)

The complex is highly hygroscopic and decompose in the presence of moisture. The magnetic susceptibility was found to be 1.58 B.M. It is lower than to be expected. This may be due to partial spin coupling. W is in (5 +) oxidation state in this complex.

Trichloro - Wolfram -V- β-Hydroxy -α- Naphthaldazine-Bis Ethandiol:

A complex was obtained in the same way as mentioned above from its components in dry dioxane.



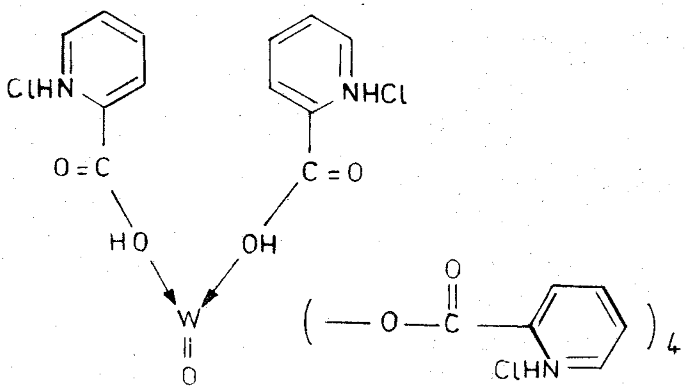
III. Orange crystalls M.P. 163°C (Decomp)

The complex is very unstable in air. Magnetic susceptibility was found to be 1.42 B.M. This is in a good agreement with the magnetic susceptibility of halide compounds of W (5+), varying from 1.52 to 1.04 B.M. by temperature (23).

The electronic configurations of both complexes can be given by d^4s hybrid configuration. d^4s hybridization shows a tetragonal pyramidal shape according to Kimball (24).

Wolfram (VI) -α- picolinic acid:

Complex was obtained from WCl_6 and α- picolinic acid in dry dioxane.



IV. Yellowish-green crystalls M.P. 215°C (Decomp)

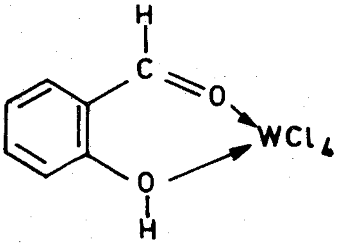
It is rather unstable in air, its colour turns to violet and is stable in water.

The magnetic susceptiblity measurements, analytical results and Infrared spectra of the complex showed that the complex is diamagnetic and its formula can be shown like number IV. But infrared spectra of the complex showed that there is no water in its structure.

So its formula should be (IV). The oxidation state of wolfram is (6+) in the complex and electronic configuration can be given by $d^5s\ p^2$ hybridisition. The shape of the complex may be like TaF_7^{-2}, which also shown $d^5s\ p^2$ hybridisition (24).

Tetrachloro-Wolfram (VI) salicylaldehyde:

A complex was prepared by heating WCl_6 and salicylaldehyde in CCl_4.



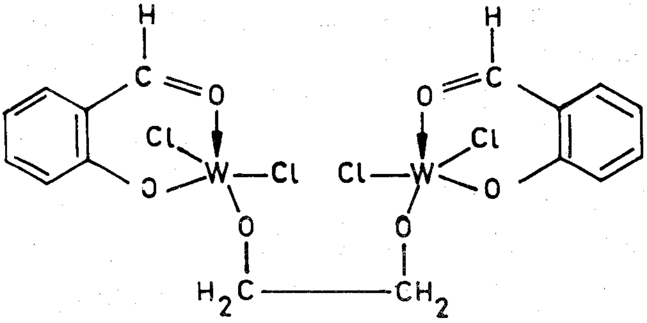
V. Black crystalls, M.P. 200°C (Decomp)

The magnetic susceptibility measurements and analytical results of the complex showed that complex is diamagnetic and its formula can be shown like number (V).

Usually it is very difficult to recrystallize these wolfram complexes because of their solubilities are too little in organic solvents and when they are heated to increase their solubility, they usually decompose to give wolfram blue (25). For that reason this complex could not be obtained as pure as desired. This was also shown by the results of elemantal analysis.

The electronic configuration of wolfram (VI) in the complex can be given by d^4s hybrid configuration which shows a threegonal prizmatic shape.

Tetrachloro-Bis Wolfram (IV) - Bis salicylaldehyde-Ethanediol: Complex was prepared by heating WCl_6 and salicylaldehyde in carbontetrachloride and dioxane.



VI. Red crystalls, M.P. 200°C (Decomp)

The complex is rather stable; the magnetic susceptibility measurements showed that complex is diamagnetic. Compounds of W (4+) usually show a magnetic momentum 0 or 2.84 B.M. depending on ligands. Some W (4+) compounds can also be paramagnetic with 2.20 B.M. (26).

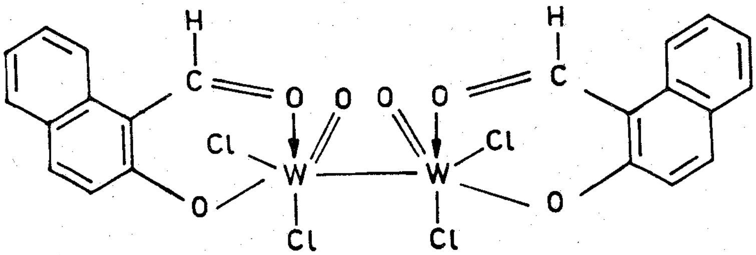
This complex has two Wolfram atoms and it is a dinuclear one. So it could be tried for nitrogen fixation (16, 17).

Because of its insolubility in organic solvents it could not be tried in homogenous medium. It was tried in heterogen medium (in CCl_4) by Warburg respirometer (27), but no result could be obtained.

The electronic configuration of Wolfram (4+) in the complex can be given by d^4s hybridization which shows a tetragonal pyramidal shape.

Tetrachloro-bis oxo di Wolfram (V) bis β- oxy α- naphthaldehyde:

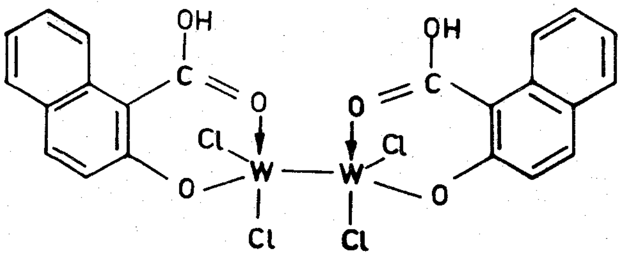
A complex was prepared with WCl_6 and β- oxy α- naphthaldehyde in carbon tetrachloride and dioxane. Complex is diamagnetic and Anayltical results confirm the formula that can be given below (VII).



VII. Black crystalls M..P 200°C (Decomp)

Wolfram is in (5+) oxidation state in this complex and diamagnetizm of the complex is due to W-W bond (28).

Although another formula (VIII) could also be given for the complex in which wolfram has (3+) oxidation state and because W—W bond complex is diamagnetic, infrared spectra shows that C—OH bond does not exist.

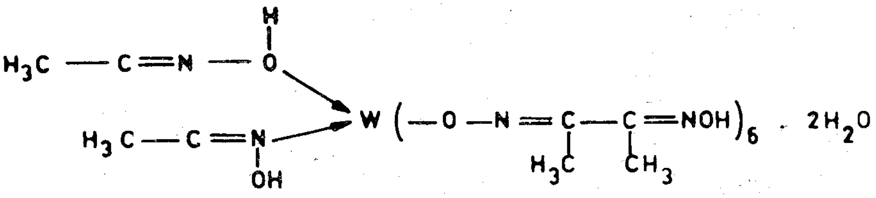


VIII. Black crystalls. M.P. 200°C (Decomp)

The electronic configuration of the complex can be given by d^5s p hybrid configuration which shows a pentagonal bipyramidal shape complexe's structure may be analog to ZrF_7^{-3}.

Wolfram (V) - bis dimethyl glyoxime:

A complex was prepared by heating WBr_5 and dimethyl glyoxime in 1,2 ethanediol with addition of some water. It is diamagnetic and according to analytical results its formula can be shown as below:



IX. Red crystalls, M.P. 200°C (Decomp)

The electronic configuration of W (5+) in the complex can be given by d^5s p^2 hybrid configuration which shows a prizmatic shape.

EXPERIMENTAL

Tetrachloro-Wolfram -V- salicylaldazine-bis ethanediol:

2 g WCl_6 is introduced into a reaction flask. 10 cc of dioxane and 2 g salicylaldazine are subsequently added and the mixture is heated and shaked slowly. When two drops of ethandiol are added drop by drop the dark colour of the solution gradually turns to light green and light green crystalls begin to accumulate at the bottom of the reaction vessel and at the same time HCl gas evolves.

The content of the vessel is left for one hour or so. Then it is filtered by sucking through a buchner funnel. The crystalls are washed twice by 5 cc of dioxane and then are put into a vacuum dessicator and dried over night.

The yield is 50 %. It decomposes at 118°C. It does not dissolve in either, carbontetrachloride, dioxane and chloroform and is slightly soluble in acetone and benzen.

After making all the structural corrections and calculations 1.58 B.M. has been found.

($C_{18}H_{23}O_6N_2Cl_4W$) (M = 687 g)

Calculated: C 31.44,	H 3.20,	O 14.00,	N 4.05,	W 26.78
Found: C 31.72,	H 3.36,	O 13.76,	N 4.16,	W 27.07

Trichloro-Wolfram -V- bis -β- Hydroxy α- Naphthaldazine Bis-Ethanediol:

2 g WCl_6 is introduced into a reaction flask. 3.56 g β-hydroxy α-naphthaldazine and 10 cc of dioxane are added and the mixture is heated under a short reflexer up to 60-70 °C and stirred. When 4 drops of ethandiol are added dropwise the solution gradually becomes red and red crystalls begin to settle down. During the reaction HCl gas evolves. Heating is continued until all of the HCl gas is driven off.

The content of the vessel is left for an hour or two. Then it is filtered by sucking through a Buchner funnel. The crystalls are washed twice by 5 cc dioxane and then are put into a vacuum dessicator and dried over night.

The yield is 80 %. M.P. 163 °C (Decomp). It does not dissolve in carbon tetrachloride, chloroform, ethyl alcohol, aceton and benzene. It hydrolysis in Dimethyl sulphoxide.

A magnetic moment of 1.42 B.M. has been found.

($C_{26}H_{22}O_6N_2Cl_3W$) (M = 753 g)

Calculated: C 41.43,	H 3.45	O 12.74	N 3.71	W 24.43
Found: C 42.08,	H 3.66,	O 13.04,	N 3.61,	W 24.40

Wolfram VI -α- picolinic acid:

1 g WCl_6 is weighed in a dried reaction vessel. 2 g of α- picolinic acid and 5 cc of dioxane are added. The mixture is heated slowly and stirred. Meanwhile the colour of the solution turns yellowish green. The reaction is completed within a short time. The content of the vessel is left for two hours, then it is quickly sucked through a buchner funnel and washed with 2 cc of dioxane and dried in a vacuum dessicator over a night.

The yield is 30 %. M.P. 215 °C (Decomp). The complex is not stable in air. It is not soluble in carbon tetrachloride and it is slightly soluble in benzene, aceton with violet colour. It is soluble in water giving a purple coloration.

Magnetic susceptibility measurements showed the complex to be diamagnetic.

$(C_{36}H_{32}O_{13}N_6Cl_6W)$ (M = 1153 g)

Calculated:	C 37.56,	H 2.78,	O 18.08,	N 7.30,	W 16.00
Found:	C 37.27,	H 3.17,	O 18.05	N 7.44,	W 16.49

Tetrachloro-Wolfram (VI) salicylaldehyde:

2 g WCl_6 is weighed in a dried reaction vessel. 1,2 g salicylaldehyde and 10 cc carbontetrachloride are added. The mixture is stirred and heated on a steam bath for an hour or two.

Black crystalls settle down on the bottom of the vessel. The content of it is left for two hours. Then is sucked through a buchner funnel and is washed with 3 cc CCl_4 for three times and dried in a vacuum dessicator over a night.

The yield is 30 %. M.P. 200 °C (Decomp).

Magnetic susceptibility measurements showed the complex to be diamagnetic.

$(C_7H_6O_2Cl_4W)$ (M = 448 g)

Calculated :	C 18.75,	H 1.33,	O 7.14,	W 41.07,
Found :	C 21.66,	H 1.46,	O 6.47,	W 40.96

Tetrachloro-Bis Wolfram (IV) - Bis salicylaldehyde-Ethandiol:

2 g WCl_6 is weighed in a dried reaction vessel. 1.2 g salicylaldehyde and the mixture of 5 cc of carbontetrachloride and 5 cc of dioxane are added. The reaction vessel is heated slowly and stirred continuously. Reddish brown crystalls settle down on the bottom of the vessel. It is left over a night. Then is sucked through a buchner funnel and is washed with 5 cc of carbontetrachloride and dried in a vacuum dessicator.

The yield is 20-30 %. M.P. 200°C (Decomp).

The complex is not soluble in ethyl alcohol, benzene, water and chloroform.

Magnetic susceptibility measurements showed the complex to be diamagnetic.

($C_{16}H_{14}O_6Cl_4W_2$) (M = 670 g)

Calculated:	C 23.66,	H 1.73,	O 11.82,	W 45.33
Found :	C 23.14,	H 2.29,	O 11.42,	W 47.02

Tetrachloro-bis oxo di Wolfram (V) bis β- oxy α- naphthaldehyde:

2 g WCl_6 and 3.4 g β- hydroxy α- naphthaldehyde are introduced into a dried reaction flask and 5 cc carbontetrachloride and 10 cc of dioxane are added. The mixture is heated slowly and stirred continously. Black crystalls begin to accumulate at the bottom of the vessel, which is left for one or two hours. Then it is sucked through a buchner funnel and washed with carbontetrachloride and dried in a vacuum dessicator over a night.

The yield is 35 %. M.P. 200°C (Decomp).

The complex is not soluble in benzene, carbontetrachloride, ethylalcohol and water. It is diamagnetic.

($C_{22}H_{14}O_6Cl_4W_2$) (M = 884 g)

Calculated:	C 29.86,	H 1.58,	O 10.85	W 41.61
Found:	C 30.27,	H 2.14,	N 10.91,	W 41.07

Wolfram (V) — bis dimethyl glyoxime:

1.5 g WBr_5 is dissolved in 15 cc of 1,2 ethanediol in a reaction vessel and the solution of 2 g dimethyl glyoxime in ethylalcohol is added into the vessel. The resulting solution which is heated slowly becomes red. When water is added dropwise into the solution dark red crystalls come out. They are sucked through a buchner funnel and washed with ethylalcohol and dried in a vacuum dessicator. They are rectystallized from 1.2 ethanediol.

The yield is 70 %. M.P. 200 °C (Decomp).

The complex is rather stable in air. It is not soluble in ethylether, carbontetrachloride, dioxan and chloroform. It is diamagnetic.

$(C_{28}H_{54}O_{16}N_{14}W)$ (M = 1026 g)

Calculated:	C 32.91,	H 5.17	N 19.12,	W 17.94
Found:	C 33.11,	H 4.82	N 19.17,	W 17.54

ÖZET

Azot tesbiti ile ilgili olarak koordinasyon kimyası alanında yapılan bu çalışmada mononükleer ve özellikle azot ile reaksiyon verme olasılığı fazla olan dinükleer wolfram kompleksleri hazırlanmağa çalışıldı. Hazırlanan kompleksler için iyi birer çözücü bulunamadığından azot tesbiti için denenemedi.

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